

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE
 in its capacity as elected Office

Date of mailing (day/month/year) 25 June 2001 (25.06.01)	
International application No. PCT/US00/20076	Applicant's or agent's file reference 500-82PCT
International filing date (day/month/year) 21 July 2000 (21.07.00)	Priority date (day/month/year) 21 July 1999 (21.07.99)
Applicant NEWBERTH, Fredrick, F., III et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 15 November 2000 (15.11.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Henrik Nyberg Telephone No.: (41-22) 338.83.38
---	---

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 600-82 PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US00/80076	International filing date (day/month/year) 21 JULY 2000	Priority date (day/month/year) 21 JULY 1998
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant LOCTITE CORPORATION		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets.

☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

I ☒ Basis of the report

II ☐ Priority

III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability

IV ☐ Lack of unity of invention

V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability, citations and explanations supporting such statement

VI ☐ Certain documents cited

VII ☐ Certain defects in the international application

VIII ☐ Certain observations on the international application

Date of submission of the demand 15 NOVEMBER 2000	Date of completion of this report 30 AUGUST 2001
Name and mailing address of the IPEA/US Comptroller of Patents and Trademarks Box PCT Washington, D.C. 20581	Authorized Officer <i>TAE H. YOON</i> TAE H. YOON
Facsimile No. (703) 305-8280	Telephone No. 703-305-2851

Form PCT/IPEA/408 (cover sheet) (July 1992)*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/20076

I. Basis of the report

1. With regard to the elements of the international application:*

☐ the international application as originally filed☒ the description:

pages (See Attached)

, as originally filed

pages , filed with the demand

pages , filed with the letter of

☒ the claims:

pages (See Attached)

, as originally filed

pages , as amended (together with any statement) under Article 19

pages , filed with the demand

pages , filed with the letter of

☒ the drawings:

pages (See Attached)

, as originally filed

pages , filed with the demand

pages , filed with the letter of

☒ the sequence listing part of the description:

pages (See Attached)

, as originally filed

pages , filed with the demand

pages , filed with the letter of

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).☐ the language of publication of the international application (under Rule 48.3(b)).☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.☐ filed together with the international application in computer readable form.☐ furnished subsequently to this Authority in written form.☐ furnished subsequently to this Authority in computer readable form.☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.4. ☒ The amendments have resulted in the cancellation of:☒ the description, pages NONE☒ the claims, Nos. NONE☒ the drawings, sheets/fig. NONE5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(o)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/0007A

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. statement

Novelty (N)	Claims 1-20	YES
	Claims NONE	NO
Inventive Step (IS)	Claims 1-20	YES
	Claims NONE	NO
Industrial Applicability (IA)	Claims 1-20	YES
	Claims NONE	NO

2. citations and explanations (Rule 70.7)

Claims 1-20 meet the criteria set out in PCT Article 33(2)-(3), because the references do not teach or suggest the instant oxylated glycerol compositions and because the instant composition is useful as an anaerobic sealant.

NEW CITATIONS

NONE

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US00/20076

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:

IPC(7): C09J 4/02, 123/06; C08K 5/053; C08L 33/06; C08F 4/04, 4/08, 220/20 and US CL. 523/176; 524/386; 526/227, 230, 236, 320, 321

I. BASIS OF REPORT:

This report has been drawn on the basis of the description,

page(s) 1-25, as originally filed.

page(s) NONE, filed with the demand,

and additional amendments:

NONE

This report has been drawn on the basis of the claims,

page(s) 29-33, as originally filed.

page(s) NONE, as amended under Article 19.

page(s) NONE, filed with the demand.

and additional amendments:

Pages 26-27 filed with the letter of 14 August 2001.

Pages 28, filed with the letter of 12 October 2001.

This report has been drawn on the basis of the drawings,

page(s) NONE, as originally filed.

page(s) NONE, filed with the demand.

and additional amendments:

NONE

This report has been drawn on the basis of the sequence listing part of the description:

page(s) NONE, as originally filed.

pages(s) NONE, filed with the demand.

and additional amendments:

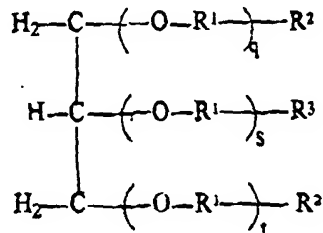
NONE

IPEA/US 14 AUG 2007

Replacement Pages
International Appl. No. PCT/US00/20076**WHAT IS CLAIMED:**

1. A free-radical curable composition which is washable and self-emulsifiable upon mixing with water comprising:

(a) a curable glycerol composition having the formula:



wherein R^1 is a substituted or unsubstituted C_1 to C_5 alkyl or combinations thereof; R^2 and R^3 are independently selected from the group consisting of hydroxyl, (meth)acrylate and combinations thereof; q, s and t are independently from about 0 to about 35; provided that at least one of said R^2 is said (meth)acrylate; at least one q, s or t, is not zero and that at least one of said R^1 is unsubstituted ethyl or unsubstituted propyl; and

(b) a free radical initiator to initiate cure of said composition.

2. The composition of claim 1 wherein said free radical initiator includes a heat-curing initiator to produce free radicals by thermal decomposition to cure said sealant.

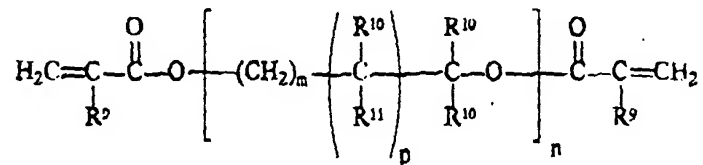
3. The composition of claim 2 wherein the heat-curing initiator is selected from the group consisting of a peroxide, a hydroperoxide, a perester, an azonitrile and combinations thereof.

4. The composition of claim 1 wherein said free radical initiator includes a anaerobic-curing initiator to produce free radicals upon the exclusion of oxygen to cure said sealant.

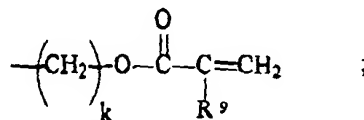
5. The composition of claim 4 wherein said anaerobic-curing initiator is a peroxy initiator selected from the group consisting of hydroperoxides, peroxides, peresters and combinations thereof.

6. The composition of claim 4 wherein said anaerobic-curing initiator includes an anaerobic accelerator selected from the group consisting of tributyl amine, benzoic sulfimide, formamide, copper octanoate and combinations thereof.

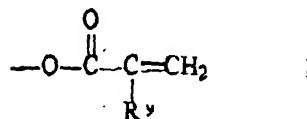
7. The composition of claim 1 further including a poly(meth)acrylate ester having the formula:



wherein R^{10} represents a radical selected from the group consisting of hydrogen, lower alkyl of from 1 to about 4 carbon atoms, hydroxyalkyl of from 1 to about 4 carbon atoms and



R^9 is a radical selected from the group consisting of hydrogen, halogen, and lower alkyl of from 1 to about 4 carbon atoms; R^{11} is a radical selected from the group consisting of hydrogen, hydroxyl and



m is 0 to about 12, n is equal to at least 1, k is 1 to about 4 and p is 0 or 1.

8. The composition of claim 1 further including a monofunctional acrylate ester, said monofunctional acrylate ester being selected from the group consisting of lauryl methacrylate, cyclohexylmethacrylate, tetrahydrofurfuryl methacrylate, hydroxyethyl acrylate,

Replacement Pages
International Appl. No. PC1/US00/20076

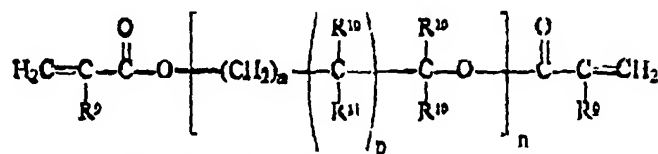
hydroxypropyl methacrylate, t-butylaminooethyl methacrylate, cyanooethylacrylate, chlorooethylmethacrylate and combinations thereof.

9. The composition of claim 1 further including an ionic surfactant, an anionic surfactant and combinations thereof.

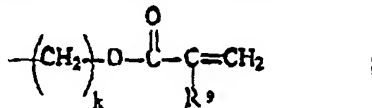
10. The composition of claim 1 wherein R^1 is ethyl, propyl or a combination thereof.

11. A free-radical curable composition which is washable and self-emulsifiable upon mixing with water comprising:

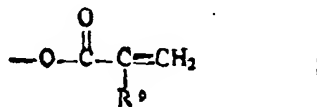
(a) a curable poly(meth)acrylate ester having the formula:



wherein R^{10} represents a radical selected from the group consisting of hydrogen, lower alkyl of from 1 to about 4 carbon atoms, hydroxyalkyl of from 1 to about 4 carbon atoms and



R^9 is a radical selected from the group consisting of hydrogen, halogen, and lower alkyl of from 1 to about 4 carbon atoms; R^{11} is a radical selected from the group consisting of hydrogen, hydroxyl and



m is 0 to about 12, n is equal to at least 1, k is 1 to about 4 and p is 0 or 1;

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

JUN 18 2001

PCT

WRITTEN OPINION

(PCT Rule 66)

To: DANIEL A. SCOLA, JR. HOFFMANN & BARON, LLP 6900 JERICO TURNPIKE SYOSSET, NY 11791		<div style="border: 2px solid black; padding: 10px; display: inline-block;"> RECEIVED JUN 19 2001 HOFFMANN & BARON, LLP </div>	Date of Mailing (day/month/year) 15 JUN 2001
Applicant's or agent's file reference 500-82 PCT			REPLY DUE within TWO months from the above date of mailing
International application No. PCT/US00/20076	International filing date (day/month/year) 21 JULY 2000	Priority date (day/month/year) 21 JULY 1999	
International Patent Classification (IPC) or both national classification and IPC Please See Supplemental Sheet.			
Applicant LOCTITE CORPORATION			

1. This written opinion is the first (first, etc.) drawn by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. ~~The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).~~

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also For an additional opportunity to submit amendments, see Rule 66.4.
 For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 *bis*.
 For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 21 NOVEMBER 2001.

Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer: TAE H. YOON
Facsimile No. (703) 305-3230	Telephone No. 703-308-2351

I. Basis of the opinion**1. With regard to the elements of the international application: ***

☒ the international application as originally filed
☒ the description:
pages 1-25 , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

☒ the claims:
pages 26-33 , as originally filed
pages NONE , as amended (together with any statement) under Article 19
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

☒ the drawings:
pages NONE , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

☒ the sequence listing part of the description:
pages NONE , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language _____ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the written opinion was drawn on the basis of the sequence listing:

- ☐ contained in the international application in printed form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

☒ the description, pages NONE
☒ the claims, Nos. NONE
☒ the drawings, sheets/fig NONE

5. ☐ This opinion has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

** Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. statement**

Novelty (N)	Claims <u>NONE</u>	YES
	Claims <u>1-20</u>	NO
Inventive Step (IS)	Claims <u>NONE</u>	YES
	Claims <u>1-20</u>	NO
Industrial Applicability (IA)	Claims <u>1-20</u>	YES
	Claims <u>NONE</u>	NO

2. citations and explanations

Claims 1-20 lack novelty and an inventive step under PCT Article 33(2)&(3) as being anticipated by, and obvious over DEMARCO who teaches the instant curable composition at column 4, lines 1-31, column 5, lines 48-66, column 8 and in table 1.

Claims 1-5, 7, 8, 10-15 and 17 lack novelty and an inventive step under PCT Article 33(2)&(3) as being anticipated by, and obvious over WATANABE et al who teach the instant curable composition at column 2, lines 1-21 and glycerin trimethacrylate in tables 1, 3 and 4.

Claims 1-8 and 11-17 lack novelty and an inventive step under PCT Article 33(2)&(3) as being anticipated by, and obvious over OZONO et al who teach the instant curable composition at column 2, line 33 to column 3, line 34, and in tables I and V.

Claims 1-8, 10-17, 19 and 20 lack novelty and an inventive step under PCT Article 33(2)&(3) as being anticipated by, and obvious over MALOFSKY et al who teach the instant curable composition at column 3, line 20 to column 4, line 35, column 5, lines 4-20 and in abstract and claims.

Claims 1, 2, 7, 8, 10-12 and 17 lack novelty and an inventive step under PCT Article 33(2)&(3) as being anticipated by, and obvious over SKOULTCHI et al who teach the instant curable composition at column 3, lines 4-51 and column 8, line 45.

Claims 1-20 meet the criteria set out in PCT Article 33(4), because the instant composition is useful as an anaerobic sealant.

----- NEW CITATIONS -----

NONE

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

WRITTEN OPINION

International application No.

PCT/US00/20076

Sup.
(To be)

I Box

when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

TIME LIMIT:

The time limit set for response to a Written Opinion may not be extended. 37 CFR 1.484(d). Any response received after the expiration of the time limit set in the Written Opinion will not be considered in preparing the International Preliminary Examination Report.

CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:

IPC(7): C09J 4/02, 133/06; C08K 5/053; C08L 33/06; C08F 4/04, 4/08, 220/20 and US Cl.: 523/176; 524/386; 526/227, 230, 236, 320, 321

IPEA/ US

PCT

CHAPTER II

DEMAND

under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only

Identification of IPEA		Date of receipt of DEMAND	
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference 500-82 PCT	
International application No. PCT/US00/20076	International filing date (day/month/year) 21 July 2000 (21.07.00)	(Earliest) Priority date (day/month/year) 21 July 1999 (21.07.99)	
Title of invention WASHABLE IMPREGNATION COMPOSITIONS			
Box No. II APPLICANT(S)			
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) LOCTITE CORPORATION 1001 Trout Brook Crossing Rocky Hill, CT 06067 US		Telephone No.: (860) 571-5001	
		Facsimile No.: (860) 571-5028	
		Teleprinter No.:	
State (that is, country) of nationality: US		State (that is, country) of residence: US	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) NEWBERTH, III, Frederick, F. 12 Greenhurst Road West Hartford, CT 06107 US			
State (that is, country) of nationality: US		State (that is, country) of residence: US	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.) CHUPAS, Peter 350 North Loop Road Schomburg Apt. #A201A Stony Brook, NY 11794 US			
State (that is, country) of nationality: US		State (that is, country) of residence: US	
<input type="checkbox"/> Further applicants are indicated on a continuation sheet.			

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is ☒ agent ☐ common representative
 and ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.
☐ is hereby appointed and any earlier appointment of (an) agent(s) /common representative is hereby revoked.
☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address: *(Family name followed by given name; for a legal entity, full official designation.
The address must include postal code and name of country.)*

SCOLA, Daniel A., Jr., et al.
 HOFFMANN & BARON, LLP
 69 Jericho Turnpike
 Syosset, NY 11791
 US

Telephone No.:
 (973) 331-1700

Facsimile No.:
 (973) 331-1717

Teleprinter No.:

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION**Statement concerning amendments:***

1. The applicant wishes the international preliminary examination to start on the basis of:

☒ the international application as originally filed
 the description ☐ as originally filed
☐ as amended under Article 34
 the claims ☐ as originally filed
☐ as amended under Article 19 (together with any accompanying statement)
☐ as amended under Article 34
 the drawings ☐ as originally filed
☐ as amended under Article 34

2. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.
 3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*
 * Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: English

☒ which is the language in which the international application was filed.
☐ which is the language of a translation furnished for the purposes of international search.
☐ which is the language of publication of the international application.
☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination.

Box No. V ELECTION OF STATES

The applicant hereby elects all eligible States *(that is, all States which have been designated and which are bound by Chapter II of the PCT)*

excluding the following States which the applicant wishes not to elect:

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

- | | | |
|--|---|--------|
| 1. translation of international application | : | sheets |
| 2. amendments under Article 34 | : | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | sheets |
| 4. copy (or, where required, translation) of statement under Article 19 | : | sheets |
| 5. letter | : | sheets |
| 6. other (<i>specify</i>) | : | sheets |

For International Preliminary Examining Authority use only

received not received

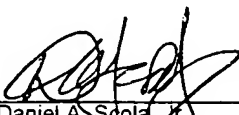
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>
<input type="checkbox"/>	<input type="checkbox"/>

The demand is also accompanied by the item(s) marked below:

- | | |
|--|---|
| 1. <input checked="" type="checkbox"/> fee calculation sheet | 4. <input type="checkbox"/> statement explaining lack of signature |
| 2. <input type="checkbox"/> separate signed power of attorney | 5. <input type="checkbox"/> nucleotide and or amino acid sequence listing in computer readable form |
| 3. <input type="checkbox"/> copy of general power of attorney, reference number, if any: | 6. <input checked="" type="checkbox"/> other (<i>specify</i>): Transmittal Letter |

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).


 Daniel A. Scola, Jr.
 Agent for Applicant

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:
2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):
3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. ☐ The applicant has been informed accordingly.
4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.
5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

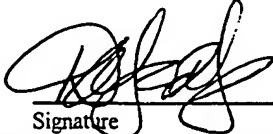
For International Bureau use only

Demand received from IPEA on:

PCT

FEE CALCULATION SHEET

Annex to the Demand for international preliminary examination

International application No. PCT/US00/20076	For International Preliminary Examining Authority use only
Applicant's or agent's file reference 500-82 PCT	Date stamp of the IPEA
Applicant LOCTITE CORPORATION	
Calculation of prescribed fees	
1. Preliminary examination fee	750.00 P
2. Handling fee <i>(Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.)</i>	153.00 H
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	<div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 0 auto;"> 903.00 </div> <div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 0 auto;"> TOTAL </div>
Mode of Payment	
<input type="checkbox"/> authorization to charge deposit account with the IPEA (see below)	<input type="checkbox"/> cash
<input checked="" type="checkbox"/> cheque	<input type="checkbox"/> revenue stamps
<input type="checkbox"/> postal money order	<input type="checkbox"/> coupons
<input type="checkbox"/> bank draft	<input type="checkbox"/> other (specify):
Deposit Account Authorization <i>(this mode of payment may not be available at all IPEAs)</i>	
The IPEA/ <u>us</u> <input type="checkbox"/> is hereby authorized to charge the total fees indicated above to my deposit account.	
<input checked="" type="checkbox"/> <i>(this check-box may be marked only if the conditions for deposit accounts of the IPEA so permit)</i> is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.	
08-2461 Deposit Account Number	13 November 2000 Date (day/month/year)
Signature 	

PCT REQUEST

500-82PCT

Original (for SUBMISSION) - printed on 21.07.2000 10:07:40 AM

0	For receiving Office use only	
0-1	International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4	Form - PCT/RO/101 PCT Request Prepared using	PCT-EASY Version 2.91 (updated 01.07.2000)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	United States Patent and Trademark Office (USPTO) (RO/US)
0-7	Applicant's or agent's file reference	500-82PCT
I	Title of invention	WASHABLE IMPREGNATION COMPOSITIONS
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	LOCTITE CORPORATION
II-5	Address:	1001 Trout Brook Crossing Rocky Hill, CT 06067 United States of America
II-6	State of nationality	US
II-7	State of residence	US
II-8	Telephone No.	860-571-5001
II-9	Facsimile No.	860-571-5028
III-1	Applicant and/or inventor	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	NEUBERTH, III, Fredrick, F.
III-1-5	Address:	12 Greenhurst Road West Hartford, CT 06107 United States of America
III-1-6	State of nationality	US
III-1-7	State of residence	US

PCT REQUEST

500-82PCT

Original (for SUBMISSION) - printed on 21.07.2000 10:07:40 AM

III-2	Applicant and/or inventor	applicant and inventor US only CHUPAS, Peter, J. 350 North Loop Road Schomburg Apt. #A201A Stony Brook, NY 11794 United States of America US US
III-2-1	This person is:	
III-2-2	Applicant for	
III-2-4	Name (LAST, First)	
III-2-5	Address:	
III-2-6	State of nationality	
III-2-7	State of residence	
IV-1	Agent or common representative; or address for correspondence The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent SCOLA, JR., Daniel, A. HOFFMANN & BARON, LLP 6900 Jericho Turnpike Syosset, NY 11791 United States of America 973-331-1700 973-331-1717 dscola@hoffmannbaron.com
IV-1-1	Name (LAST, First)	
IV-1-2	Address:	
IV-1-3	Telephone No.	
IV-1-4	Facsimile No.	
IV-1-5	e-mail	
IV-2	Additional agent(s)	additional agent(s) with same address as first named agent ABBRUZZESE, Salvatore, J.; BARON, Mark, E.; MERKEL, Kellyanne; SOPKO, John, S.; JACOBSEN, Barry, H.; SZAKIEL, Gloria, K.; LANGE, Keith, R.; CUSICK, Clinton, J.; HOFFMANN, Charles, R.; BARON, Ronald, J.; BODNER, Gerald, T.; SACK, Alan, M.; KAMMER, A., Thomas; SCHROEDER, R., Glenn; HENNEBERGER, Glenn, T.; FEIT, Irving, N.; BENNETT, Anthony, E.; BACHMANN, Gregory, W.; ZUSCHLAG, Steven, T.; SIPOS, Susan, A.; MCDERMOTT, Kevin, E.; MORRISS, Robert, C.; TURNER, Roderick, S., W.; HARRINGTON, James, F.; LACAVA, Richard; ANILIONIS, Algis; HOLMES, Justin, K.; BERNSTEIN, Robert, L.
IV-2-1	Name(s)	
IV-3	Additional agent(s)	agent BAUMAN, Steven, C. 1001 Trout Brook Crossing Rocky Hill, CT 06067 United States of America 860-571-5001 860-571-5028
IV-3-1	Name (LAST, First)	
IV-3-2	Address:	
IV-3-3	Telephone No.	
IV-3-4	Facsimile No.	

PCT REQUEST

500-82PCT

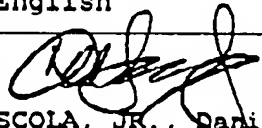
Original (for SUBMISSION) - printed on 21.07.2000 10:07:40 AM

V	Designation of States	
V.1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	<p>AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT</p> <p>EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT</p> <p>EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT</p> <p>OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT</p>
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	<p>AF AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&LI CN CR CU CZ DE DK DM DZ EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW</p>
V-3	<p>Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-3 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.</p>	
V-4	Exclusion(s) from precautionary designations	NONE
VI-1	Priority claim of earlier national application	
VI-1-1	Filing date	21 July 1999 (21.07.1999)
VI-1-2	Number	60/144,896
VI-1-3	Country	US
VI-2	<p>Priority document request The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s):</p>	
		VI-1

PCT REQUEST

500-82PCT

Original (for SUBMISSION) - printed on 21.07.2000 10:07:40 AM

VII-1	International Searching Authority Chosen	United States Patent and Trademark Office (USPTO) (ISA/US)	
VIII	Check list	number of sheets	electronic file(s) attached
VIII-1	Request	5	-
VIII-2	Description	25	-
VIII-3	Claims	8	-
VIII-4	Abstract	1	-
VIII-5	Drawings	0	-
VIII-7	TOTAL	39	
	Accompanying items	paper document(s) attached	electronic file(s) attached
VIII-8	Fee calculation sheet	✓	-
VIII-9	Separate signed power of attorney	✓	-
VIII-10	Copy of general power of attorney	✓	-
VIII-16	PCT-EASY diskette	-	diskette
VIII-17	Other (specified):	Assignment	-
VIII-17	Other (specified):	Combined Declaration and Power of Attorney	-
VIII-17	Other (specified):	Check	-
VIII-17	Other (specified):	Stamped Return Postcard	-
VIII-18	Figure of the drawings which should accompany the abstract		
VIII-19	Language of filing of the international application	English	
IX-1	Signature of applicant or agent		
IX-1.1	Name (LAST, First)	SCOLA, JR., Daniel, A.	

FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/US
10-6	Transmittal of search copy delayed until search fee is paid	

PCT REQUEST

5/5

500-82PCT

Original (for SUBMISSION) - printed on 21.07.2000 10:07:40 AM

FOR INTERNATIONAL BUREAU USE ONLY

11.1	Date of receipt of the record copy by the International Bureau	
------	---	--

PCT (ANNEX - FEE CALCULATION SHEET)

500-82PCT

Original (for SUBMISSION) - printed on 21.07.2000 10:07:40 AM

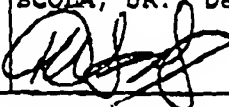
(This sheet is not part of and does not count as a sheet of the international application)

0	For receiving Office use only	
0-1	International Application No.	
0-2	Date stamp of the receiving Office	
0-4	Form - PCT/RO/101 (Annex) PCT Fee Calculation Sheet Prepared using	PCT-EASY Version 2.91 (updated 01.07.2000)
0-3	Applicant's or agent's file reference	500-82PCT
2	Applicant	LOCTITE CORPORATION, et al.
12	Calculation of prescribed fees	fee amount/multiplier total amounts (USD)
12-1	Transmittal fee T	240
12-2	Search fee S	700
12-3	International fee	
	Basic fee (first 30 sheets) b1	427
12-4	Remaining sheets 9	
12-5	Additional amount (X) 10	
12-6	Total additional amount b2	90
12-7	b1 + b2 = B	517
12-8	Designation fees	
	Number of designations contained in International application 87	
12-9	Number of designation fees payable (maximum 8) 8	
12-10	Amount of designation fee (X) 92	
12-11	Total designation fees D	736
12-12	PCT-EASY fee reduction R	-132
12-13	Total International fee (B+D-R) I	1,253
12-14	Fee for priority document	
	Number of priority documents requested 1	
12-15	Fee per document (X) 15	
12-16	Total priority document fee P	15
12-17	TOTAL FEES PAYABLE (T+S+I+P)	2,208
12-18	Mode of payment	cheque
12-20	Deposit account instructions The receiving Office:	United States Patent and Trademark Office (USPTO) (RO/US)
12-20-2	is hereby authorized to charge any deficiency or credit any over-payment in the total fees indicated above to my deposit account	✓
12-20-3	is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account	✓

PCT (ANNEX - FEE CALCULATION SHEET)

500-82PCT

Original (for SUBMISSION) - printed on 21.07.2000 10:07:40 AM

12-31	Deposit account No.	08-2461
12-42	Date	21 July 2000 (21.07.2000)
12-23	Name and signature	SCOLA, JR. Daniel, A. 

VALIDATION LOG AND REMARKS

13-7-6	Validation messages Contents	Yellow The abstract should be attached in electronic form.
		Green? The international application contains no drawings. Please verify.
		Green? Reference number for attached copy of general power of attorney not indicated.
13-2-7	Validation messages Fees	Green? Please confirm that fee schedule utilized is the latest available
		Green? Int'l fee: PCT-EASY reduction has not been applied as the abstract has not been attached in electronic form on the Contents page.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
1 February 2001 (01.02.2001)

PCT

(10) International Publication Number
WO 01/07530 A1

(51) International Patent Classification⁷: C09J 4/02,
133/06, C08K 5/053, C08L 33/06, C08F 4/04, 4/08,
220/20

(74) Agents: SCOLA, Daniel, A., Jr.; Hoffmann & Baron,
LLP, 6900 Jericho Turnpike, Syosset, NY 11791 et al.
(US).

(21) International Application Number: PCT/US00/20076

(22) International Filing Date: 21 July 2000 (21.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/144,896 21 July 1999 (21.07.1999) US

(71) Applicant (for all designated States except US): LOC-
TITE CORPORATION [US/US]; 1001 Trout Brook
Crossing, Rocky Hill, CT 06067 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (for US only): NEWBERTH,
Fredrick, F., III [US/US]; 12 Greenhurst Road, West
Hartford, CT 06107 (US). CHUPAS, Peter, J. [US/US];
350 North Loop Road, Schomburg Apt. #A201A, Stony
Brook, NY 11794 (US).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: WASHABLE IMPREGNATION COMPOSITIONS

(57) Abstract: Anaerobic and heat curing polymerizable impregnation compositions for sealing porous articles are disclosed. The compositions contain glycerol, oxygenated glycerol or (meth)acrylate glycerol to improve the washability of the compositions in aqueous solutions. The compositions may contain other compounds to effect the curing characteristics of the sealants.

WO 01/07530 A1

WASHABLE IMPREGNATION COMPOSITIONS

FIELD OF THE INVENTION:

The present invention relates generally to washable, polymerizable compositions. More particularly, the present invention relates to such compositions curable through mechanisms, anaerobic, and heat curing for use as impregnation sealants.

5 BRIEF DESCRIPTION OF RELATED TECHNOLOGY:

Impregnation sealing of porosity in porous parts frequently is carried out by introducing sealant compositions into the porosity under a pressure differential, by vacuum techniques which are well known in the art.

10 Sealant compositions typically employed in these impregnation applications include a wide variety of self-curing anaerobic sealants, e.g., the compositions described in U.S. Patent Nos. 3,672,942; 3,969,552; Re. 32,240; and 4,632,945, which are curable through free-radical polymerization in the presence of suitable free-radical initiators, e.g., peroxy-type initiators, as well as thermal-curing sealants, e.g., the compositions described in U.S. Patent Nos.
15 4,416,921 and 4,416,921, as well as sealants which cure by both anaerobic and heat cure mechanisms.

One problem common to many impregnation sealants is the accumulation of excess sealant on the outer surface of parts. Excess sealant is removable by normal abrasion or by
20 contact with various liquids. The removal of extraneous or surface accumulation of anaerobic and heat curing sealants from the parts is important because such residues can readily contaminant the environment of porous parts. In addition, such surface sealant deposits may, by virtue of their thickness, cause the impregnated product part to vary from the desired dimensional specifications. This often renders the part deficient or even useless for its
25 intended function in applications requiring close dimensional tolerances.

Furthermore, such surface sealant deposits may interfere with subsequent painting,

plating, or assembly operations or cause delamination of applied paint or plated films which frequently are performed on porous articles subsequent to their impregnation. Specifically, such surface sealant deposits may be removed during painting or plating operations, resulting in contamination of the baths used in such operations, and may interfere with the adhesion of paint, plating, and the like to the impregnated part.

To remove excess sealant from impregnated articles, agitated rinse times of significant duration are required. The actual rinse time will depend upon, among other things, the nature of the article, such as porosity, and the washability of the uncured sealant in an aqueous solution. Often such rinse operations are from about five to about twenty minutes, but actual rinse times may for any particular article may be even longer in duration. In addition, chemicals, such as surfactants or detergents, may also be added to the aqueous solution to facilitate the removal of sealant deposits.

For example, U.S. Patent No. 3,672,942 to Neumann et al. discloses an anaerobic impregnant comprising a free-radical polymerizable acrylate ester monomer and free-radical polymerization initiator, which requires an organic solvent, such as a halogenated hydrocarbon, to remove uncured impregnant from the outer surface of a porous article.

U.S. Patent No. 3,969,552 to Malofsky et al. describes a washing process for removing excess impregnant from the surface of the porous article after porosity impregnation. The disclosed impregnation composition comprises an acrylic anaerobic curing resin and a peroxy initiator therefor. The wash solution is an aqueous solution of a nonionic surfactant of specified formula which is necessary for the removal of uncured impregnant.

U.S. Patent No. Re. 32,240 to DeMarco describes a self-emulsifying anaerobic composition for porosity impregnation applications, comprising an anaerobically curing monomer such as an acrylic ester, a peroxy initiator therefor, e.g., a hydroperoxide or prester, an anionic or nonionic surfactant which is dissolved in the composition and renders

it self-emulsifying upon mixing with water.

U.S. Patent No. 5,256,450 to Catena describes an anaerobic polymerizable acrylate composition which requires a mixture of three different polymerizable acrylates in specific amounts to obtain a composition that cures and rinses without the use of organic solvents or surfactants.

The above-described anaerobic sealant compositions are typically impregnated into the porosity of metal parts by vacuum and pressure techniques. A vacuum removes air from the porosity of the metal parts. Sealant compositions are then introduced into the porosity under a pressure differential using ambient pressure or elevated pressure conditions. After impregnation, an operation, such as a centrifuge operation, removes excess surface sealant from the metal part. Even after such removal of gross surface accumulations of the impregnant, there is a significant amount of impregnant at the surface of the porous articles, particularly in the vicinity of the pores. When the impregnant is anaerobically cured, the aforementioned surface accumulations as well as the outermost layer of the impregnant in the pores of the article, particularly shallow surface pores, are in contact with oxygen, so that such surface quantities of the impregnant are uncured or only partially cured.

Remaining surface sealant or sealant trapped in blind holes of the impregnated parts is typically removed in an agitated water rinse zone. The impregnated and water-rinsed parts may be transferred to an activator zone in which the impregnated parts are contacted with a catalyst activator solution, to effect curing of the sealant material at the entrance to the pores in the parts. This creates a hardened plug or cap of sealant material in the outer portion of the pore, trapping the resin for anaerobic self-cure.

Thereafter, the impregnated parts may be transferred to a final rinse zone for removal of the activator solution from the impregnated parts. This final rinse solution may be at elevated temperature, e.g., on the order of about 50°C, to warm the impregnated parts for quick drying, and to accelerate curing of the anaerobic impregnant within the interior porosity

of the article, the rate of such cure increasing with increasing temperature.

As a variation on the above-described impregnation system, it is known to utilize a heat-curing resin in place of the anaerobically-curing resin, whereby the activating and final rinsing steps previously described are eliminated in favor of a hot rinse final step. In the heat-curing resin impregnation system, after impregnation and rinsing of excess surface material, the parts are contacted with hot water at temperatures on the order of about 50°C to about 90°C to cure the impregnant resin.

Among the previously developed heat-curing impregnating compositions for sealing porous parts are the compositions disclosed in the patents identified and discussed below.

U.S. Patent No. 4,416,921 to Dunn describes a heat-curing sealant composition which contains a polymerizable acrylic monomer, an azonitrile and a anionic or nonionic surfactant to render the composition self-emulsifying upon mixing with water.

U.S. Patent No. 4,147,821 to Young describes a heat-curing sealant composition which contains (meth)acrylic monomer and a polyfunctional acrylic monomer. An emulsifier is required to aid in the rinsing of uncured sealant from the surface of a porous article.

Once the heat-curable impregnant composition is introduced into the porosity of the parts to be sealed, the parts are transferred to an agitated water rinse zone for removal of any remaining surface accumulations of sealant or extraneous sealant which is trapped in blind holes of the impregnated parts. After removal of the excess sealant in the agitated water rinse zone, the impregnated parts are passed to a tank containing hot water, e.g., at a temperature of 90°C to 150°C, or other medium at elevated temperature which serves to cure the sealant composition in the porosity. Relative to anaerobic impregnant compositions, heat-curable impregnant compositions may be effectively used with a minimum of monitoring and maintenance, with little or no aeration being required.

In all of the above-described impregnation compositions and systems, either organic solvents or specific surfactants are used to remove uncured sealant in a reasonable rinse time or specific multi-component sealant compositions are used to avoid excessive rinse times.

5 Accordingly, there is a need to provide a heat-curable and/or an anaerobic impregnating sealant without these and other disadvantages.

SUMMARY OF THE INVENTION:

10 The present invention provides washable compositions for sealing porous articles which have improved washability characteristics and reduced rinsing requirements. The present compositions achieve lower rinse times while producing improved surface cleaning of uncured polymer. The compositions of the present invention demonstrate utility in the sealing and/or aqueous rinsing operations, and obviate the conventional use of multi-component cleaning systems.

15 In particular, the present invention provides a sealant composition with improved washability, thereby reducing the rinse duration, improved ease of use by eliminating the need for specific surfactants, and which improve surface cleanliness of the porous article.

20 In one embodiment of the present invention, the inventive composition includes a curable (meth)acrylate glycerol, and is self-emulsifying upon mixing with water to facilitate aqueous rinsing of uncured composition. The inventive composition further includes curing initiators and curing accelerators to promote anaerobic or thermal curing through free radical mechanisms.

25 In another embodiment of the present invention, the invention composition includes a polymerizable composition and further includes a compound selected from the group consisting of glycerol, oxylated glycerol, (meth)acrylate glycerol and combinations thereof which improve the washability of the inventive sealants in aqueous solutions.

In one desirable embodiment, the inventive composition contains an (meth)acrylate glycerol which has at least one terminal (meth)acrylate group to allow crosslinking of the (meth)acrylate glycerols upon curing.

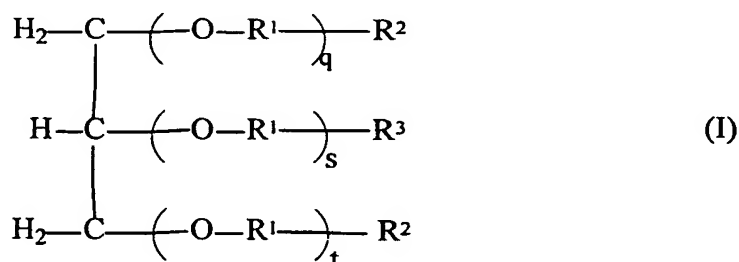
5 **DETAILED DESCRIPTION OF THE INVENTION:**

The present invention is directed to a sealant composition with improved washability characteristics as compared to known sealant compositions. The present invention provides sealant compositions, the components of which serve to provide washability and self-emulsificability to the overall composition. These components may be included with the
10 inventive sealant composition during the impregnation operation or may be incorporated during the water rinse operation to provide washability and self-emulsificability to the overall composition. Uncured sealant is typically removed from the surface of the porous article during the aqueous rinse portion of the sealing process. As used herein the term "washable" and its variants refer to the ability of a sealant composition to emulsify in an aqueous solution
15 and be readily removed from unwanted areas of an article in the aqueous solution. Also, as used herein the term "self-emulsificability" and its variants refer to the ability of one liquid to form minute droplets in a second liquid resulting in a heterogeneous mixture of two liquid phases.

20 The present compositions employ an independent component selected from the group consisting of glycerol, oxylated glycerol, (meth)acrylate glycerol and combinations thereof as an additive to anaerobic or heat curable polymerizable compositions. The polymerizable composition includes polyfunctional and monofunctional (meth)acrylate esters to effectuate the polymerizable properties of the sealant. The inventive sealant compositions may contain
25 other components to tailor the polymerizing, curing or emulsifying properties of the compositions. The inventive sealants also contain an initiator system and/or inhibitor systems to provide controlled anaerobic or thermal curing mechanisms. These compositions have a variety of uses, including an impregnation compositions, sealants, adhesives, coatings and the like. One particularly desirable embodiment relates to impregnation sealant
30 compositions for porous parts.

The inventive compositions are generally curable by free-radical mechanisms. Typically, anaerobic conditions or elevated temperature condition may be used. In impregnation applications, however, generally anaerobic and/or thermal mechanisms are used. Furthermore, the inventive compositions are self-emulsifying upon mixing with water to facilitate the aqueous rinsing of an impregnated article.

In one embodiment of the inventive composition the washability and self-emulsificability enhancing component in the form of glycerol is incorporated into the resultant polymer backbone. This composition includes a curable (meth)acrylate glycerol component having the formula:



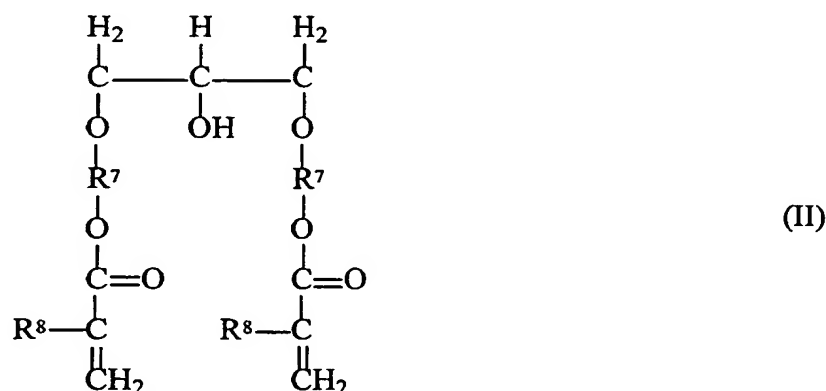
wherein R¹ is a substituted or unsubstituted C₁ to C₅ alkyl or a combination thereof, R² and R³ are independently selected from the group consisting of hydroxyl, (meth)acrylate and combinations thereof, provided that at least one R² is a (meth)acrylate, where q, s and t are independently from about 0 to about 35; and a free radical initiator component or system for producing free radicals to initiate cure of said composition. The short chain C₁ to C₅ alkyl groups, as compared to longer chain alkyl groups, assist in the washability of the inventive compositions. Longer chain alkyl groups can act negatively to retard emulsification. Desirably, R¹ is an ethyl, a propyl or combinations thereof. The (meth)acrylate glycerol compositions produce cross-linked polymers upon curing which serve as effective and durable self-washing sealants. The free radical initiator component provides free radicals for both anaerobic or heat curing of the composition.

The inventive compositions may contain from about 50% to about 99%

(meth)acrylate glycerol by weight of the total composition with the balance including other materials, for instance, initiators, inhibitors, surfactants, inerts, for instance, non-reactive plasticizers, and the like.

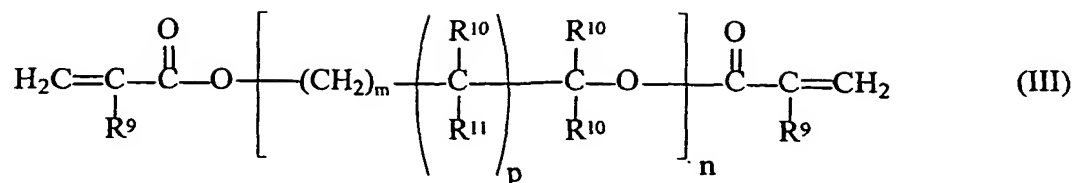
- 5 The (meth)acrylate glycerol compositions may be suitably prepared by condensing hydroxyalkyl (meth)acrylate, such as hydroxyethyl(meth)acrylate (HEMA), onto hydroxyl groups of an oxylated glycerol, such as an oxylated glycerol of formula VI below.

- 10 In an alternate embodiment, the inventive compositions include a self-washing polymerizable di(meth)acrylate glycerol having the formula:

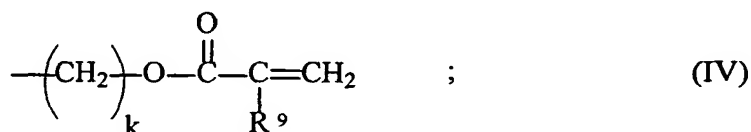


wherein R⁷ is an ethyl or propyl alkyl and R⁸ is hydrogen or methyl; and a free radical initiator component or system.

- 15 Furthermore, in still another embodiment the inventive sealant composition may include at least one crosslinkable polymer, a curing component for said polymer and a compound selected from the group consisting of glycerol, oxylated glycerol, (meth)acrylate glycerol and combinations thereof. Desirably, the polymerizable component has a majority of polyfunctional (meth)acrylate esters (hereinafter, poly(meth)acrylate esters). These
- 20 polyfunctional esters produce cross-linked polymers, which serve as effective and durable sealants, adhesives and coatings. While various (meth)acrylate esters may be used, desirable poly(meth)acrylate esters include those with the following general formula:

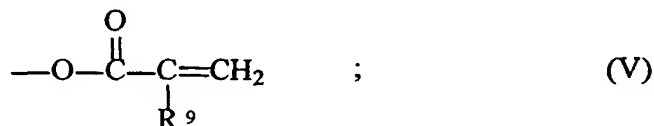


wherein R^{10} represents a radical selected from the group consisting of hydrogen, lower alkyl of from 1 to about 4 carbon atoms, hydroxyalkyl of from 1 to about 4 carbon atoms and



5

R^9 is a radical selected from the group consisting of hydrogen, halogen, and lower alkyl of from 1 to about 4 carbon atoms; R^{11} is a radical selected from the group consisting of hydrogen, hydroxyl, and



10 and m may be 0 to 12, and desirably from 0 to about 6; n is equal to at least 1, e.g., 1 to about 20 or more, and desirably between about 2 to about 6; k is 1 to about 4; and p is 0 or 1.

The polymerizable poly(meth)acrylate esters corresponding to the above general formula are exemplified by, but not restricted to, the following materials: di-, tri- and
 15 tetraethyleneglycol dimethacrylate, dipropyleneglycol dimethacrylate; polyethyleneglycol dimethylacrylate (PEGMA); di(pentamethyleneglycol) dimethacrylate; tetraethyleneglycol diacrylate; tetraethyleneglycol di(chloracrylate); diglycerol diacrylate; diglycerol tetramethacrylate; tetramethylene dimethacrylate; ethylene dimethacrylate; and neopentylglycol diacrylate. Combinations and derivatives of these polyfunctional materials
 20 are contemplated.

Monofunctional (meth)acrylate esters (esters containing one (meth)acrylate group) are also advantageously used in the present compositions. The most common of these monofunctional esters include the alkyl esters such as lauryl methacrylate. Many of the lower molecular weight alkyl esters are quite volatile, and frequently it is more desirable to use a higher molecular weight homolog, such as decyl methacrylate or dodecyl methacrylate, or any other fatty acid acrylate esters, in (meth)acrylate-based impregnant compositions.

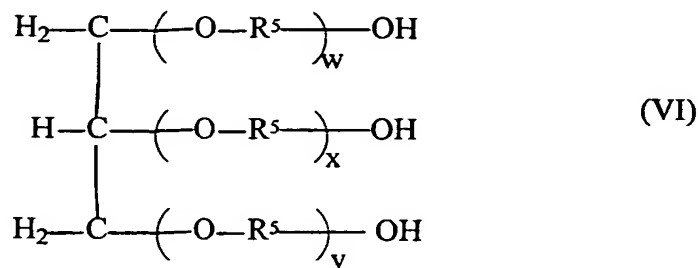
When monofunctional (meth)acrylate esters are employed in the present compositions, it is desirable to use an ester which has a relatively polar alcohol moiety. Such materials are less volatile than low molecular weight alkyl esters and, in addition, the polar group tends to provide intermolecular attraction in the cured polymer, thus producing a more durable seal. Desirably the polar group is selected from the group consisting of labile hydrogen, heterocyclic ring, hydroxy, amino, cyano, and halogen polar groups. Typical examples of compounds within this category are cyclohexylmethacrylate, tetrahydrofurfuryl methacrylate, hydroxyethyl acrylate (HEMA), hydroxypropyl methacrylate (HPMA), t-butylaminoethyl methacrylate, cyanoethylacrylate, and chloroethylmethacrylate. Combinations of monofunctional (meth)acrylate are contemplated.

When poly(meth)acrylate esters and monofunctional (meth)acrylate esters are employed together in the present compositions, the ratio of poly(meth)acrylate esters to monofunctional (meth)acrylate esters on a weight basis is generally about 0.05:1 to about 20:1. Desirably, for use in impregnation compositions the ratio is about 5:1. Furthermore, the inventive curable (meth)acrylate glycerol compounds can be combined with such esters in amounts of about 0.1% to about 99% by weight of the total composition. In other words, the washability of such esters can be improved by combining various amounts of (meth)acrylate glycerol.

In yet another embodiment of the present invention, a glycerol or an oxylated glycerol is combined with polymerizable sealant compositions to further improve washability thereof. The oxylated glycerol may be incorporated into the sealant composition or may be added

separately into the aqueous rinse solution used to wash the sealant compositions thereby aiding in the removal of uncured surface and extraneous sealant from the surface of the part.

The oxylated glycerols of the present invention have the formula:



wherein R^5 is a substituted or unsubstituted C_1 to C_5 alkyl or a combination thereof and w , x and y are independently from about 0 to about 35. Desirably, R^5 is an ethyl, a propyl or combinations thereof.

When poly(meth)acrylate esters and monofunctional (meth)acrylate esters are employed together in the present compositions, the ratio of poly(meth)acrylate esters to monofunctional (meth)acrylate esters on a weight basis is generally about 0.05:1 to about 20:1. Desirably, for use in impregnation compositions the ratio is about 5:1. Furthermore, the inventive oxylated glycerols can be combined with such esters in amounts of about 0.1% to about 75% by weight of the total composition. In other words, the washability of such esters can be improved by combining various amounts of oxylated glycerols.

The compositions of the present invention may be anaerobically curable through a free-radical mechanism, with an initiator being present therein, or an initiator system comprising a redox polymerization initiator (i.e., an ingredient or a combination of ingredients which produce an oxidation-reduction reaction, resulting in the production of free radicals). Suitable initiators include peroxy materials e.g., peroxides, hydroperoxides, and peresters, which are capable of inducing polymerization of the inventive compositions in the substantial absence of oxygen, and yet not induce polymerization as long as oxygen is present. Organic hydroperoxides are the desirable peroxy materials with t-butyl

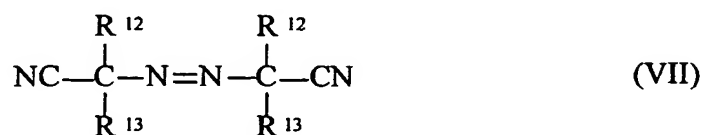
hydroperoxide and cumene hydroperoxide being particularly useful with the inventive compositions.

In addition to initiator components, the composition of the present invention may include various initiator accelerators, as for example hydroperoxide decomposition accelerators, when hydroperoxides are used as cure initiators in the sealant material. Typical examples of potentially suitable accelerators include: tertiary amines such as tributyl amine; sulfimides such as benzoic sulfimide (or saccharin); formamide; and compounds containing transition metals, such as copper octanoate.

The inventive compositions may also be heat-curable compositions through a free-radical mechanism, with a heat-cure initiator being present therein, or an initiator system comprising a redox polymerization initiator (i.e., an ingredient or a combination of ingredients which at the desired elevated temperature conditions, e.g. from about 90° to about 150°C, produce an oxidation-reduction reaction, resulting in the production of free radicals). Suitable initiators may include peroxy materials, e.g., peroxides, hydroperoxides, and peresters, which under appropriate elevated temperature conditions decompose to form peroxy free radicals which are initiatingly effective for the polymerization of the inventive compositions.

Another useful class of heat-curing initiators comprises azonitrile compounds which yield free radicals when decomposed by heat. Heat is applied to cure the composition, and the resulting free radicals initiate polymerization of the inventive composition.

For example, azonitrile may be a compound of the formula:



wherein R¹² is a methyl, ethyl, n-propyl, iso-propyl, iso-butyl or n-pentyl radical, and R¹³ is a

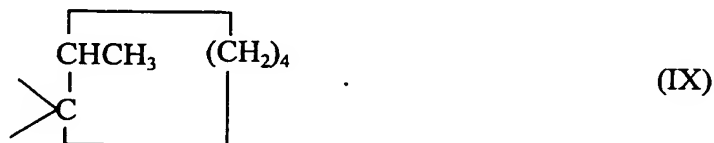
methyl, ethyl, n-propyl, iso-propyl, cyclopropyl, carboxy-n-propyl, iso-butyl, cyclobutyl, n-pentyl, neo-pentyl, cyclopentyl, cyclohexyl, phenyl, benzyl, p-chlorbenzyl, or p-nitrobenzyl radical or R^{12} and R^{13} , taken together with the carbon atom to which they are attached, represent a radical of the formula

5



wherein m is an integer from 3 to 9, or the radical

10



Compounds of the above formula are more fully described in U.S. Patent No. 4,416,921, the disclosure of which hereby is incorporated herein by reference.

15

Azonitrile initiators of the above-described formula are readily commercially available, e.g., the initiators which are commercially available under the trademark VAZO® from E. I. DuPont de Nemours and Company, Inc. (Wilmington, Del.), including VAZO® 52 (R^{12} =methyl, R^{13} =isobutyl), VAZO® 64 (R^{12} =methyl, R^{13} =methyl), and VAZO® 67 (R^{12} =methyl, R^{13} =ethyl), all such R^{12} and R^{13} constituents being identified with reference to the

20

A desirable azonitrile initiator is 2,2'-azobis(iso-butyronitrile) or AZBN.

The azonitrile may be employed in the inventive heat-curable compositions in concentrations on the order of about 500 to about 10,000 parts per million (ppm) by weight, desirably about 1000 to about 5000 ppm.

25

Other (meth)acrylic monomer-based impregnant compositions of a heat-curable character may be employed in the broad practice of the present invention, including those disclosed in UK Patent Specifications 1,308,947 and 1,547,801. As described in these

30

references, the monomeric impregnant composition may contain suitable inhibitors serving to restrict or preclude the occurrence of polymerization of the monomer, at temperatures below those desired or recommended for heat-curing of the impregnant composition.

5 The inventive impregnant compositions may also contain other constituents, such as:
other co-monomer species, reactive diluents, pigments, surfactants, fillers, polymerization
inhibitors, stabilizers, anti-oxidants, anti-corrosion additives, and the like. For example,
surfactants may be combined with the inventive compositions or included in the aqueous
rinse solution. The use of surfactants and specific materials utilized for such purpose are
10 more fully described in U.S. Patent No. 3,969,552 and Re. 32,240, the disclosures of each of
which are expressly incorporated herein by reference. Suitable surfactants include classes of
anionic surfactants, such as petroleum sulfonates, alkyl sulfonates or alkylaryl sulfonates and
nonionic surfactants, such as, ethoxylated alkyl phenols, ethoxylated linear secondary
alcohols, polyoxyethylene or polyoxypropylene glycols.

15

The invention may be further understood with reference to the following non-limiting
examples. Percent weights are per the total composition unless otherwise specified.

EXAMPLES

Example 1

- 5 An anaerobic sealant composition according to the present invention (Composition One) was prepared with the following formulation:

Table 1

<u>Composition One</u>	<u>WT %</u>
Triethyleneglycol dimethacrylate	74.00
Lauryl methacrylate	15.00
Hydroxpropyl methacrylate	5.00
Surfactant	5.24
Fluorescence	0.02
Inhibitor	0.04
Benzosulfimide (saccharin)	0.30
t-butyl hydroperoxide	<u>0.40</u>
Total:	100.00

- 10 A lapshear, such as a metal lapshear (1" x 4" x 1/16") in accordance with ASTM D-1002, was coated with the above inventive composition. The coated lapshear was repeatedly dipped into room temperature tap water to clean the coated lapshear to yield a base dipping requirement to clean the lapshear. Glycerol dimethacrylate was then combined with inventive Composition One at various levels as shown below and the cleaning procedure was repeated.
- 15 As illustrated in the below results in Table 2, including glycerol dimethacrylate in the Composition One increased the washability thereof, as evidenced in a decrease in dips required for cleaning. These compositions proved to have particular efficacy as an impregnation composition.

Table 2

<u>Glycerol Dimethacrylate Incorporated into Inventive Composition One, WT%</u>	<u>Number of Dips into 27°C Tap Water to Clean Coated Lapshear</u>
0	50+
1	35
3	35
5	35
7	25
9	20
15	20

Example 2

5

An anaerobic sealant composition according to the present invention (Composition Two) was prepared with the following formulation:

Table 3

<u>Composition Two</u>	<u>WT %</u>
Butanediol dimethacrylate	50.00
Triallyl Cyanurate	30.00
Lauryl methacrylate	19.04
Fluorescence	0.02
Inhibitor	0.04
Saccharin	0.30
70% t-butyl hydroperoxide	<u>0.60</u>
Total:	100.00

A lapshear, as described above in Example 1, was coated with the above composition.

- 10 The coated lapshear was repeatedly dipped into room temperature tap water to clean the coated lapshear to yield a base dipping requirement to clean the lapshear. Glycerol dimethacrylate was then combined with inventive Composition Two at various levels as shown below and the cleaning procedure was repeated. As illustrated in the results below, incorporating glycerol dimethacrylate in the composition increased the washability thereof, as
- 15 evidenced by the decrease in number of dips required for cleaning. These compositions

proved to have particular efficacy as an impregnation composition.

Table 4

<u>Glycerol Dimethacrylate Incorporated into Inventive Composition Two, WT%</u>	<u>Number of Dips into 27°C Tap Water to Clean Coated Lapshear</u>
0	50+
1	15
3	13
5	10
7	8
9	8

Example 3

5

The anaerobic sealant composition (Composition Two) of Example 2 was used in the following washability study.

A lapshear, as described above in Example 1, was coated with the above composition.

- 10 The coated lapshear was repeatedly dipped into room temperature tap water to clean the coated lapshear to yield a base dipping requirement to clean the lapshear. Ethoxylated glycerol was then combined with the sealant composition at various levels as shown below and the cleaning procedure was repeated. As illustrated in the below results in Table 5, including ethoxylated glycerol in the composition increased the washability thereof, as
- 15 evidenced by a decrease in the number of dips required for cleaning. These compositions proved to have particular efficacy as an impregnation composition.

Table 5

<u>Ethoxylated Glycerol Incorporated into Inventive Composition Two, WT%</u>	<u>Number of Dips into 27°C Tap Water to Clean Coated Lapshear</u>
0	50+
1	40
3	20
5	13
7	13
9	10

Example 4

5

The anaerobic sealant composition (Composition Two) of Example 2 was used in the following washability study.

10 A lapshear, as described above in Example 1, was coated with the above sealant composition. The coated lapshear was repeatedly dipped into room temperature tap water to clean the coated lapshear to yield a base dipping requirement to clean the lapshear. Propoxylated glycerol was then combined with the sealant composition at various levels as shown below and the cleaning procedure was repeated. As illustrated in the below results in Table 6, including propoxylated glycerol in the sealant composition increased the washability thereof, as evidenced by a decrease in the number of dips required for cleaning. These
15 compositions proved to have particular efficacy as an impregnation composition.

Table 6

<u>Propoxylated Glycerol Incorporated into Inventive Composition Two, WT%</u>	<u>Number of Dips into 27°C Tap Water to Clean Coated Lapshear</u>
0	50+
1	17
3	15
5	12
7	10
9	10

Example 5

An anaerobic sealant composition according to the present invention (Composition Three) was prepared with the following formulation:

Table 7

<u>Inventive Composition Three</u>	<u>Anaerobic Sealant, WT %</u>
Glycerol dimethacrylate	97.0
cumene hydroperoxide	<u>3.0</u>
Total:	100.0

Two drops, or about 0.4 grams, of the inventive composition was placed on a lapshear, as described in Example 1. A second lapshear was placed over the inventive composition, and the two lapshears were clamped together. A fixture test was then preformed at periodic time intervals. For the fixture test the two lapshears were unclamped at a particular time period. If the lapshears could move relative to one and the other, the inventive composition did not fully cure. The two lapshear would be reclamped until the next time interval. If the two unclamped lapshears could not moved relative to one and the other, then the inventive composition did fully cure. As illustrated below results in Table 8, the inventive composition anaerobically cured and proved to have particular efficacy as an impregnation composition with improved washability characteristics.

Table 8

<u>Inventive Composition Three</u>	<u>Room Temperature Anaerobic Curing</u>
1 hour after assembly	Not Cured
2 hours after assembly	Not Cured
3 hours after assembly	Not Cured
4 hours after assembly	Fully Cured

Example 6

- 5 An anaerobic sealant composition according to the present invention (Composition Four) was prepared with the following formulation:

Table 9

<u>Inventive Composition Four</u>	<u>Anaerobic Sealant, WT %</u>
Glycerol dimethacrylate	96.7
cumene hydroperoxide	3.0
Benzosulfimide (saccharin)	<u>0.3</u>
Total:	100.0

- 10 Two drops, or about 0.4 grams, of the inventive composition was used for a fixture test, as described in Example 5, with two lapshears. Saccharin proved to be an effective accelerator for aerobically curing the inventive composition. As illustrated below results in Table 10, the inventive composition anaerobically cured and proved to have particular efficacy as an impregnation composition with improved washability characteristics.

Table 10

<u>Inventive</u> <u>Composition Four</u> 1 hour after assembly	<u>Room</u> <u>Temperature</u> <u>Anaerobic Curing</u> Fully Cured
--	---

Example 7

An anaerobic sealant composition according to the present invention (Composition
5 Five) was prepared by adding 1 gram of copper octanoate to 100 grams of Inventive
Composition Four of Example 6. Two drops, or about 0.4 grams, of the inventive
composition was used for a fixture test, as described in Example 5, with two lapshears.
Copper octanoate proved to be an effective accelerator for aerobically curing the inventive
composition. As illustrated below results in Table 11, the inventive composition anaerobically
10 cured and proved to have particular efficacy as an impregnation composition with improved
washability characteristics.

Table 11

<u>Inventive</u> <u>Composition Five</u> 20 minutes after assembly	<u>Room</u> <u>Temperature</u> <u>Anaerobic Curing</u> Fully Cured
--	---

Example 8

An anaerobic sealant composition according to the present invention (Composition Six) was prepared with the following formulation:

5

Table 12

<u>Inventive Composition Six</u>	<u>Anaerobic Sealant, WT %</u>
Glycerol dimethacrylate	77.0
Lauryl methacrylate	10.0
Hydroxpropyl methacrylate	10.0
cumene hydroperoxide	<u>3.0</u>
Total:	100.0

Two drops, or about 0.4 grams, of the inventive composition was used for a fixture test, as described in Example 5, with two lapshears. As illustrated below results in Table 13, the inventive composition anaerobically cured and proved to have particular efficacy as an impregnation composition with improved washability characteristics.

10

Table 13

<u>Inventive Composition Six</u>	<u>Room Temperature Anaerobic Curing</u>
1 hour after assembly	Not Cured
2 hours after assembly	Not Cured
3 hours after assembly	Not Cured
4 hours after assembly	Not Cured
5 hours after assembly	Not Cured
6 hours after assembly	Not Cured
7 hours after assembly	Partially Cured

Example 9

An heat curable sealant composition according to the present invention (Composition Seven) was prepared with the following formulation:

Table 14

Inventive <u>Composition Seven</u>	Heat Curable Sealant, <u>WT %</u>
Glycerol dimethacrylate	97.0
cumene hydroperoxide	<u>3.0</u>
Total:	100.0

Two drops, or about 0.4 grams, of the inventive composition was placed on a lapshear, as described in Example 1. A second lapshear was placed over the inventive composition, and the two lapshears were clamped together. The assembly was placed in an oven and maintained at 121°C. A fixture test, as described in Example 5, was then preformed after one hour. As illustrated below results in Table 15, the inventive composition thermally cured at 121°C and proved to have particular efficacy as an impregnation composition with improved washability characteristics.

Table 15

Inventive <u>Composition Seven</u> 1 hour after assembly	121 °C <u>Heat Curing</u> Fully Cured
--	---

Example 10

A heat curable sealant composition according to the present invention (Composition

Eight) was prepared with the following formulation:

Table 16

<u>Inventive Composition Eight</u>	<u>Heat Curable Sealant, WT %</u>
Glycerol dimethacrylate	96.7
cumene hydroperoxide	3.0
Benzosulfimide (saccharin)	<u>0.3</u>
Total:	100.0

Two drops, or about 0.4 grams, of the inventive composition was used for a fixture test, as described in Example 9, with two lapshears. As illustrated below results in Table 17, the inventive composition thermally cured at 121°C and proved to have particular efficacy as an impregnation composition with improved washability characteristics.

Table 17

<u>Inventive Composition Eight</u> 1 hour after assembly	<u>121°C Heat Curing</u> Fully Cured
---	---

Example 11

A heat curable sealant composition according to the present invention (Composition Nine) was prepared with the following formulation:

Table 18

<u>Inventive Composition Nine</u>	<u>Heat Curable Sealant, WT %</u>
Glycerol dimethacrylate	77.0
Lauryl methacrylate	10.0
Hydroxypropyl methacrylate	10.0
cumene hydroperoxide	<u>3.0</u>
Total:	100.0

Two drops, or about 0.4 grams, of the inventive composition was used for a fixture test, as described in Example 9, with two lapshears. As illustrated below results in Table 19, the inventive composition thermally cured at 121°C and proved to have particular efficacy as an impregnation composition with improved washability characteristics.

Table 19

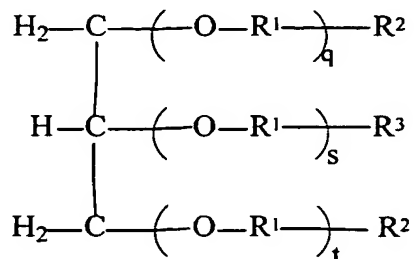
<u>Inventive Composition Nine</u> 1 hour after assembly	<u>121°C Heat Curing</u> Fully Cured
--	---

The invention being thus described, it will be clear to those persons of skill in the art that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention and all such modifications are intended to be included within the scope of the claims.

WHAT IS CLAIMED IS:

1. A free-radical curable composition which is washable and self-emulsifiable upon mixing with water comprising:

5 (a) a curable glycerol composition having the formula:



wherein R¹ is a substituted or unsubstituted C₁ to C₅ alkyl or combinations thereof; R² and R³ are independently selected from the group consisting of hydroxyl, (meth)acrylate and combinations thereof; q, s and t are independently from about 0 to about 35; provided that at
 10 least one of said R² is said (meth)acrylate; and

(b) a free radical initiator to initiate cure of said composition.

2. The composition of claim 1 wherein said free radical initiator includes a heat-
 15 curing initiator to produce free radicals by thermal decomposition to cure said sealant.

3. The composition of claim 2 wherein the heat-curing initiator is selected from the group consisting of a peroxide, a hydroperoxide, a perester, an azonitrile and combinations thereof.

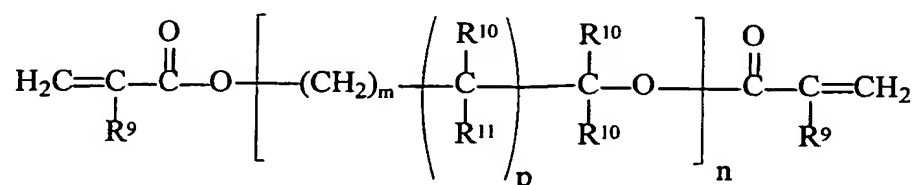
20

4. The composition of claim 1 wherein said free radical initiator includes a anaerobic-curing initiator to produce free radicals upon the exclusion of oxygen to cure said sealant.

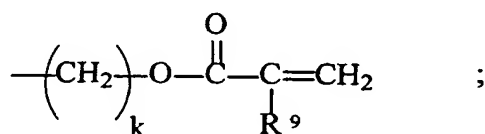
5. The composition of claim 4 wherein said anaerobic-curing initiator is a peroxy initiator selected from the group consisting of hydroperoxides, peroxides, peresters and combinations thereof.

6. The composition of claim 4 wherein said anaerobic-curing initiator includes an anaerobic accelerator selected from the group consisting of tributyl amine, benzoic sulfimide, formamide, copper octanoate and combinations thereof.

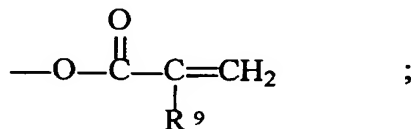
7. The composition of claim 1 further including a poly(meth)acrylate ester having the formula:



wherein R^{10} represents a radical selected from the group consisting of hydrogen, lower alkyl of from 1 to about 4 carbon atoms, hydroxyalkyl of from 1 to about 4 carbon atoms and



R^9 is a radical selected from the group consisting of hydrogen, halogen, and lower alkyl of from 1 to about 4 carbon atoms; R^{11} is a radical selected from the group consisting of hydrogen, hydroxyl and



m is 0 to about 12, n is equal to at least 1, k is 1 to about 4 and p is 0 or 1.

8. The composition of claim 1 further including a monofunctional acrylate ester, said monofunctional acrylate ester being selected from the group consisting of lauryl

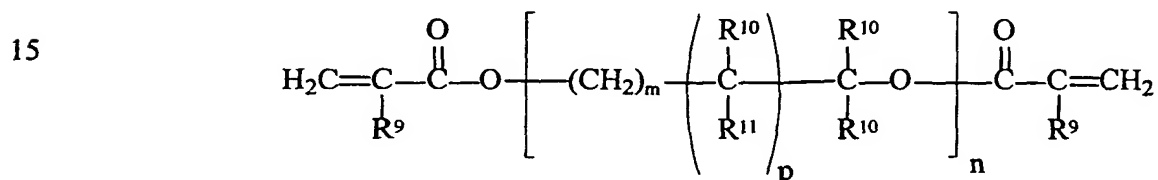
methacrylate, cyclohexylmethacrylate, tetrahydrofurfuryl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, t-butylaminoethyl methacrylate, cyanoethylacrylate, chloroethylmethacrylate and combinations thereof.

5 9. The composition of claim 1 further including an ionic surfactant, an anionic surfactant and combinations thereof.

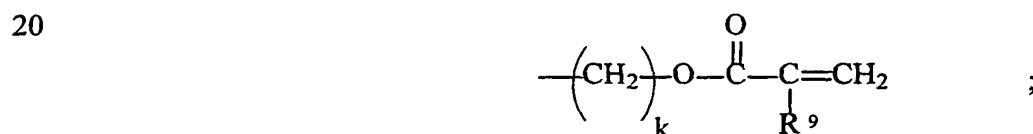
10 10. The composition of claim 1 wherein R¹ is ethyl, propyl or a combination thereof.

11. A free-radical curable composition which is washable and self-emulsifiable upon mixing with water comprising:

(a) a curable poly(meth)acrylate ester having the formula:

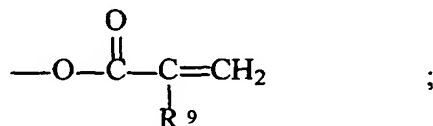


wherein R¹⁰ represents a radical selected from the group consisting of hydrogen, lower alkyl of from 1 to about 4 carbon atoms, hydroxyalkyl of from 1 to about 4 carbon atoms and



R⁹ is a radical selected from the group consisting of hydrogen, halogen, and lower alkyl of from 1 to about 4 carbon atoms; R¹¹ is a radical selected from the group consisting of

25 hydrogen, hydroxyl and

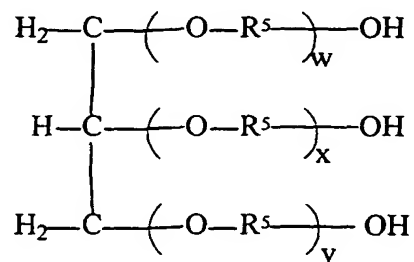


m is 0 to about 12, n is equal to at least 1, k is 1 to about 4 and p is 0 or 1;

30

(b) a washing agent for emulsifying said curable poly(meth)acrylate ester, said washing agent is selected from the group consisting of a glycerol composition, a (meth)acrylate glycerol composition and combinations thereof; wherein

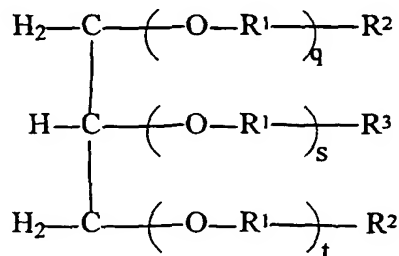
(i) said glycerol composition having the formula:



5

wherein R^5 is a C_1 to C_5 substituted or unsubstituted alkyl or a combination thereof; w , x and y are independently from 0 to about 35; and

(ii) said (meth)acrylate glycerol composition having the formula:



10 wherein R^1 is a substituted or unsubstituted C_1 to C_5 alkyl or combinations thereof; R^2 and R^3 are independently selected from the group consisting of hydroxyl, (meth)acrylate and combinations thereof; q , s and t are independently from about 0 to about 35; provided that at least one of said R^2 is said (meth)acrylate; and

15 (c) a free radical initiator for producing free radicals to initiate cure said composition.

12. The composition of claim 11 wherein said free radical initiator includes a heat-curing initiator to produce free radicals by thermal decomposition to cure said composition.

13. The composition of claim 12 wherein the heat-curing initiator is selected from the group consisting of a peroxide, a hydroperoxide, a perester, an azonitrile and combinations thereof.

5 14. The composition of claim 11 wherein said free radical initiator includes a anaerobic-curing initiator to produce free radicals upon the exclusion of oxygen to cure said sealant

10 15. The composition of claim 14 wherein said anaerobic-curing initiator is a peroxy initiator selected from the group consisting of hydroperoxides, peroxides, peresters and combinations thereof.

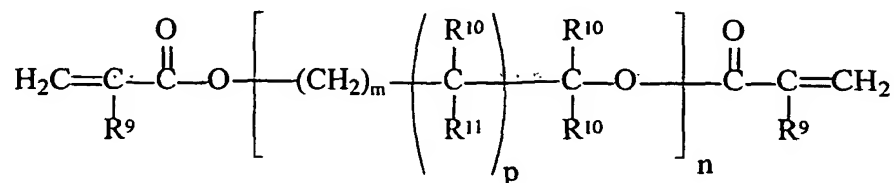
15 16. The composition of claim 14 wherein said anaerobic-curing initiator includes an anaerobic accelerator selected from the group consisting of tributyl amine, benzoic sulfimide, formamide, copper octanoate and combinations thereof.

20 17. The composition of claim 11 further including a monofunctional acrylate ester, said monofunctional acrylate ester being selected from the group consisting of lauryl methacrylate, cyclohexylmethacrylate, tetrahydrofurfuryl methacrylate, hydroxyethyl acrylate, hydroxypropyl methacrylate, t-butylaminoethyl methacrylate, cyanoethylacrylate, chloroethylmethacrylate and combinations thereof.

18. The composition of claim 11 further including an ionic surfactant, an anionic surfactant and combinations thereof.

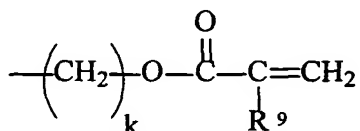
19. A method for washing uncured anaerobic or heat curing sealant from a surface from an article comprising:

(a) impregnating said article with a curable poly(meth)acrylate ester having the formula:



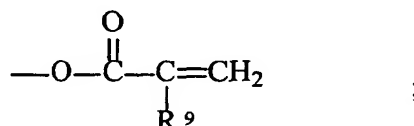
5

wherein R^{10} represents a radical selected from the group consisting of hydrogen, lower alkyl of from 1 to about 4 carbon atoms, hydroxyalkyl of from 1 to about 4 carbon atoms and



R^9 is a radical selected from the group consisting of hydrogen, halogen, and lower alkyl of from 1 to about 4 carbon atoms; R^{11} is a radical selected from the group consisting of hydrogen, hydroxyl and

10

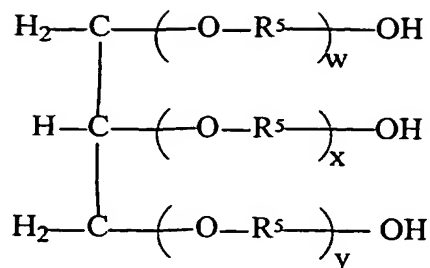


15 m is 0 to about 12, n is equal to at least 1, k is 1 to about 4, and p is 0 or 1;

(b) adding a washing agent for emulsifying said curable poly(meth)acrylate ester into a wash tank containing an aqueous solution, said washing agent is selected from the group consisting of a glycerol composition, a (meth)acrylate glycerol composition and combinations thereof; wherein

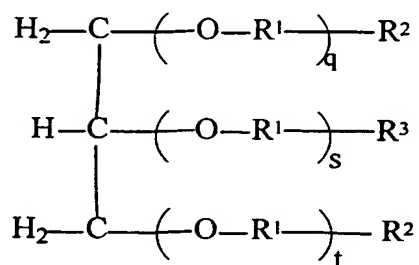
20

(i) said glycerol composition having the formula:



wherein R^5 is a substituted or unsubstituted C_1 to C_5 alkyl or a combination thereof; w, x and y are independently from about 0 to about 35 and

(ii) said (meth)acrylate glycerol composition having the formula:



5

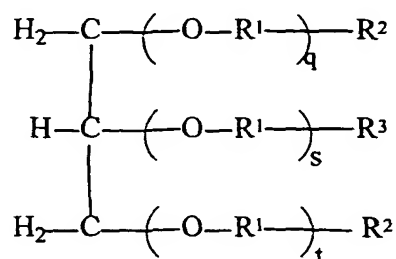
wherein R^1 is a substituted or unsubstituted C_1 to C_5 alkyl or combinations thereof; R^2 and R^3 are independently selected from the group consisting of hydroxyl, (meth)acrylate and combinations thereof; q, s and t are independently from about 0 to about 35; provided that at least one of said R^2 is said (meth)acrylate; and

10

(c) washing said curable poly(meth)acrylate ester from the surface of said article in said wash tank containing said aqueous solution and said washing agent.

20. A method of anaerobically or thermally sealing a porous article comprising:

(a) selecting a curable glycerol composition having the formula:



wherein R¹ is a substituted or unsubstituted C₁ to C₃ alkyl or combinations thereof; R² and R³ are independently selected from the group consisting of hydroxyl, (meth)acrylate and combinations thereof; q, s and t are independently from about 0 to about 35; provided that at least one of said R² is said (meth)acrylate; and

(b) selecting a free radical initiation to initiate curing of said curable glycerol;

(c) impregnating pores of said article with said curable glycerol and said initiator, and

(d) washing said curable glycerol from a surface of said article in a wash tank containing an aqueous solution.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/20076

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : Please See Extra Sheet.

US CL : 523/176; 524/386; 526/227, 230, 236, 320, 321

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/176; 524/386; 526/227, 230, 236, 320, 321

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST; glycerol, glycerin, anaerobic, diacrylate, dimethacrylate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,651,036 A (WATANABE et al) 21 March 1972, col. 2, lines 1-21 and glycerin trimethacrylate in tables 1, 3 and 4.	1-5, 7, 8, 10-15, 17.
X	US 3,775,385 A (OZONO et al) 27 November 1973, col. 2, line 33 to col. 3, line 34 and tables I and V.	1-8, 11-17.
X	US 3,969,552 A (MALOFSKY et al) 13 July 1976, abstract, col. 3, line 20 to col. 4, line 35, col. 5, lines 4-20 and claims.	1-8, 10-17, 19, 20.
X	US 4,602,073 A (SKOULTCHI et al) 22 July 1986, col. 3, lines 4-51 and col. 8, line 45.	1, 2, 7, 8, 10-12, 17.

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

03 OCTOBER 2000

Date of mailing of the international search report

30 OCT 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

TAE H. YOON

Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/20076

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US Re 32,240 A (DEMARCO) 02 September 1986, col. 4, lines 1-31, col. 5, lines 48-66, col. 8 and table 1.	1-20

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/20076

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (7):

C09J 4/02, 133/06; C08K 5/053; C08L 33/06; C08F 4/04, 4/08, 220/20